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Sensors for direct methanol fuel cells

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ABSTRACT

A sensor can be used to enhance the performance of a direct methanol fuel cell (DMFC). Sensors function as alarms for various problems encountered with DMFCs, of which methanol crossover is the primary problem. These sensors can significantly improve DMFC operation, thereby promoting the commercialisation of this product. Using sensors can also lower DMFC fabrication costs. For all of these reasons, an overview of sensor applications for DMFCs is presented in this paper. Different types of sensors and advances in sensor development are also discussed, particularly for DMFC systems. Finally, this paper highlights current issues and future improvements for the application of sensors to DMFCs.

Contents

1. Introduction

DMFCs are potential mobile and stationary power sources because of their high energy densities, easy operation and simple fuel supply requirements. However, methanol crossover is typically encountered with DMFCs, particularly for fuels with high methanol concentrations. Methanol solution is mixed with water and used as fuel for DMFCs. DMFCs do not require fuel storage and are therefore easy to handle. DMFCs can be microminiaturised because their operating temperatures are low [1–3]. A sensor is a device that responds to a physical stimulus, such as heat, light, sound, pressure, magnetism, or a particular motion, and outputs an impulse for measurement purposes or to operate a control. Sensors are critical in fuel cells for various tasks, such as detecting the fuel concentration and carbon monoxide emissions. Currently, the most popular sensors for overcoming the aforementioned problems are methanol concentration sensors, temperature sensors, humidity sensors, carbon monoxide detection sensors and

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flow sensors. Sensor-less approaches have also been used to determine the best method for upgrading DMFC efficiency and performance. Sensors for fuel cells can be classified into two main categories, which are based on the sensing mode employed: electrochemical sensors and physical sensors [4].

1.1. Electrochemical sensors

Electrochemical sensors can convert methanol concentrations into readable electrical signals via the electrochemical oxidation of methanol. These sensors are simple structures that are easy to operate and low in cost; however, problems such as the deterioration of the catalytic surface may arise during sensor operation. These sensor types are constructed similarly to DMFCs and are based on polymer electrode membranes (Zhao et al. [5]. Electrochemical sensors can be further classified into sensors based on fuel cells and those that use an oxidant current. In a fuel-cell-based sensor, the methanol concentration is determined by the measurement of operating characteristics, such as the open-circuit voltage and the short-circuit current, or the operating voltage for a constant resistor load. This type of sensor requires a continuous supply of oxidant to the cathode [6]. The second type of methanol sensor measures diffusion-limited concentration-dependent oxidation current of methanol at the anode under a constant applied voltage [5]. The associated reactions are given below.

The overall reaction for methanol oxidation is given as follows:

$$CH_3OH + H_2O \rightarrow CO_2 + 6e^- + 6H^+ \text{ (anode)} \quad (1)$$

The reaction for the fuel-cell-based sensor is as follows:

$$5O_2 + 6e^- + 6H^+ \rightarrow 3H_2O \text{ (cathode)} \quad (2)$$

The reaction for the sensor that uses an oxidation current is as follows:

$$6H^+ + 6e^- \rightarrow 3H_2 \text{ (cathode)} \quad (3)$$

1.2. Physical sensors

Physical sensors employ physical methods to measure physical properties such as the density, the viscosity, the infrared light transmittance, the dielectric constant, the refractive index, the heat capacity, or the speed of sound [5]. These sensors must be used with an auxiliary driving device and additional sensors, such as a thermometer or optical sensors [2,7]. Physical sensors are difficult to handle because of their bulky size and temperature dependence. These sensors also have a complex structure and are difficult to miniaturise [2]. Sung et al. fabricated an ultrasonic transducer to monitor and control the methanol concentration (see Fig. 1). However, this transducer produces results that do not agree with theoretical models, which predict that the speed of sound decreases as the temperature increases. Doerner et al. [9] subsequently fabricated a sensor for measuring the methanol concentration (see Fig. 2). The measurement technique uses impedance spectrum analyser electronics, which can be used under process conditions. Fig. 3 shows the position of the methanol sensor for a schematic of a direct methanol fuel cell (DMFC) power plant.

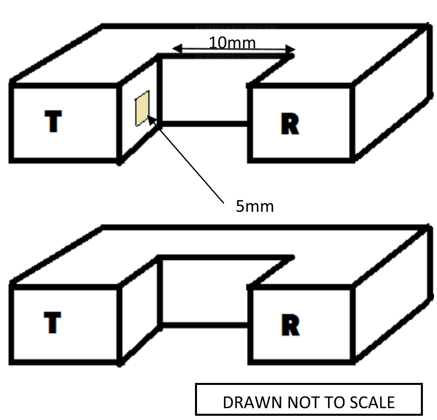


Fig. 1. Transducer in sensing methanol concentration [8].

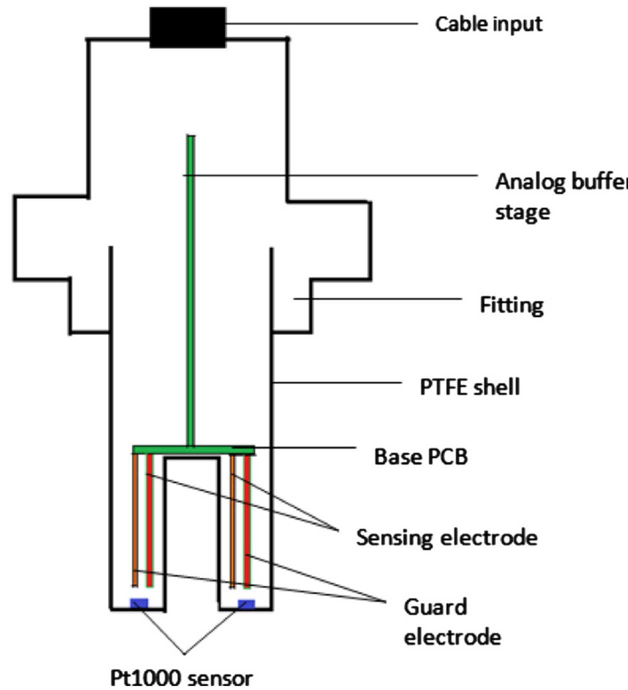


Fig. 2. Design of capacitive sensor; immerse probe [9].

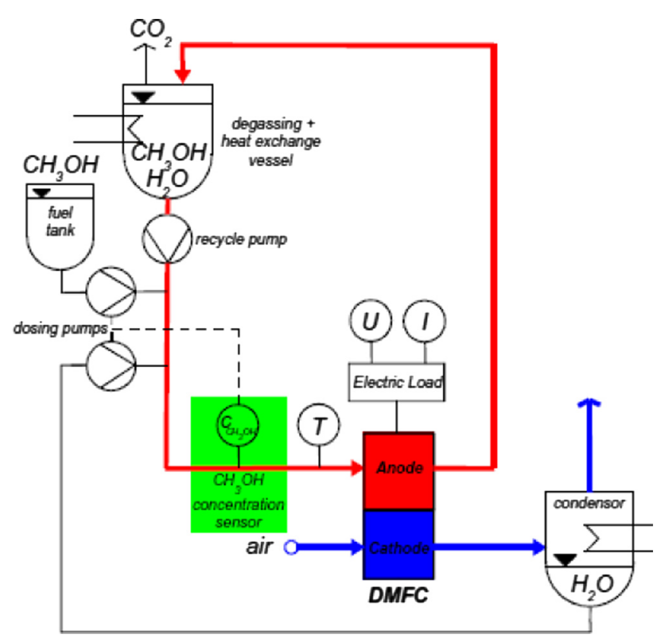


Fig. 3. Location of methanol sensor in the schematic diagram of DMFC power plant [9].

2. Nanomaterial-based electrode for sensors

Nano analytical sensing systems that use noble metals have started to attract attention because they can effectively catalyse redox processes, while providing a larger surface area for reaction, are eco-friendly and can output easy-to-read data [10,11]. Research in this area has been limited to platinum nanoparticles and carbon nanotubes and will be described further in the next section. Nanotechnologies can be adapted to enhance the performance of sensing materials applications. The small sizes of nano-materials can increase the sensing surface area of certain materials, thereby reducing the amount of material required for loading. Platinum is expensive and difficult to obtain; therefore, reducing the Pt load can promote the commercialisation of DMFCs. Using noble metal materials (NMNs), such as Pt, Pd, Ag and Au, can also greatly enhance fuel cell efficiency. Pt and Pt-based nanomaterials are primarily used as effective catalysts in DMFCs [10]. Unfortunately, Pt is difficult to obtain and expensive. Such material considerations contribute to the high cost and somewhat slow market growth of DMFCs, despite all of the advantages they have to offer. Thus, research studies have been conducted to identify suitable non-Pt materials with the same characteristics as Pt.

In a notable research study, Park et al. [12] developed a stable methanol concentration detector using a platinum (Pt) nanoparticle modified electrode coated with a silicon epoxy (SE) film. The SE film was used to eliminate the adsorption of carbon monoxide (CO) onto the Pt electrode. The sensor was stable over 40 h of repeated operation, and the SE film completely eliminated CO adsorption. Lee et al. [13,14] fabricated a sensor in which the methanol concentration was cycled to produce changes in the resistance, while changes in the conductance were realised using sensing materials composed of Nafion-coated single-walled carbon nanotube (SWCNT) composite films on a pair of inter-digitated electrodes (see Fig. 4). Cycling the methanol concentration from 0.5 M to 5 M produced changes in the resistance of the sensor, while the changes in the sensor conductance were realised by using different methanol concentrations in water.

Later, Tay et al. fabricated unique hybrid nano-particles with a silica core and a densely grafted oligomeric ionomer layer, which was synthesised via atom transfer radical polymerisation (ATRP) and incorporated into the Nafion, thereby improving the proton conductivity and lowered the methanol permeability by a factor of four [15]. Zhiani et al. [16] demonstrated that for DMFC applications, modifying Pt/C particle surfaces with polyaniline nanofibres (PANI) produced more effective anode catalyst (PANI/Pt/C) than unmodified Pt/C nanoparticles for methanol electrooxidation. Moghaddam and Pickup [18] found that using Ru oxide and PANI as supports in methanol oxidation did not significantly affect the reaction. Dulal et al. [17] subsequently developed a stable electrode by electrodepositing platinum nanoparticles on a carbon fibre, which produced a higher intensity peak in the cyclic voltammogram than for bare carbon. This study also showed that the particle size significantly affected the methanol oxidation reaction. Kun et al. [19] fabricated an electrochemical propranolol hydrochloride (PRO) sensor by combining Pt nanoparticles with multi-walled carbon nanotubes (CNTs). The oxidation peaks were found to increase in intensity as the quantity of Pt/CNT was increased. Table 1 summarised the description of sensors.

3. Current development of DMFC sensors

3.1. Methanol concentration sensor

Methanol concentration sensors are used in both fuel-cell-based sensors and those that use an oxidant current, as previously discussed. Methanol concentrations ranging from 0 M to 5 M (pure methanol) are usually used in normal DMFC operation. Low methanol concentrations require a container with a large volume, which cannot be accommodated by existing DMFC system designs. High methanol concentrations also correspond to a high energy density and increase the potential for methanol crossover [7,20]. Several research studies have shown that increasing the thickness of the methanol barrier layer decreases the methanol crossover [20,21]. High methanol concentrations also trigger methanol saturation. Methanol crossover also can be affected by the temperature. At low density of the solution, increasing the temperature has the same effect as increasing the methanol

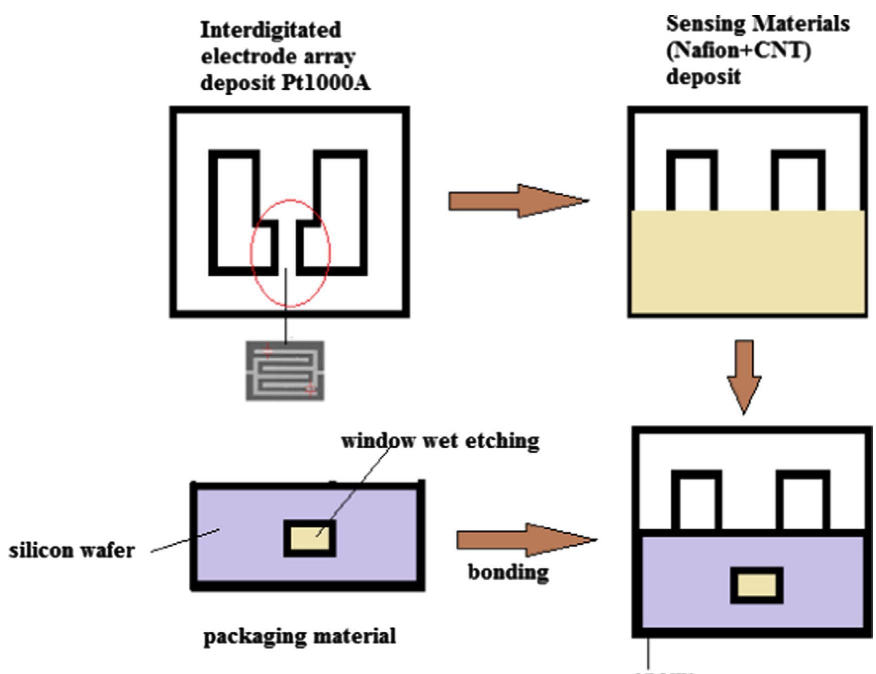


Fig. 4. Fabrication of Nafion coated single wall carbon nanotubes (SWCNT) films as sensor [13].

Table 1
Summarised the description of sensors.

No.	Materials for electrode	Purpose	Advantages	Technique
1.	Pt coated with silicon epoxy (Park et al. [12])	Methanol concentration sensor	Adsorption of CO to electrode is eliminated Detection: 1.0×10^{-4} M	Double potential step chroroamperometry
2.	Nafion coated SWCNT (Lee et al. [13])	Methanol concentration sensor	Nafion easily transport methanol Detection: 0.5–5 M	Resistance response
3.	PANI/Pt/C (Zhiani et al. [16])	Methanol oxidation	PANI nanofibers may remove CO from surface of catalyst	Chroroamperometry
4.	MWCNT/Pt (Kun et al. [19])	Propranolol hydrochloride (PRO) sensor	Good linear relationship between the anodic peak current and PRO concentration. The detection limit of PRO sensor 8.45 × 10 – 8 M.	Differential pulse voltammogram (DPV)
5.	Pt/Ppy-graphene (Park and Kim [43])	Electrochemical analysis for catalyst	Graphene increase the utilization of Pt	Cyclic voltametry
6.	Pt–C/Pt–Ru (Kamarudin et al., 2009) [44]	Catalyst for DMFC	PtRu can resist poisonous CO	Cyclic voltametry
7.	Pt-Ppy	Methanol oxidation (Bouzek and Ju, 2001) [45]	High catalytic activity observed when using Pt deposited onto pre-synthesised Ppy film.	Cyclic voltametry

Nos.	Author	Sensing material	Description	Speciality	Disadvantages
1.	Jeng et al.	Methanol	Detection: 0–4 M Operating temperature: 20–80 °C	Smaller anode, converge site of reaction	Expensive Pt–C as sensing materials Obstruction in gas flow
2.	Geng et al.		Detection: 0–2 M Operating temperature: 30–60 °C	Self-cleaning of the surface of electrode	Stationary, not portable
3.	Yan et al.		Detection: 0–5 M (2.5 M) Operating temperature: 30–60 °C	Mini size sensor coupled with DMFC	Sensitivity approaches the sufficient value, but not satisfactory
4.	Lee et al.		Detection: 0.5–3 M Operating temperature: 80 °C	Mini-size, low power, no GDL	No GDL, bubbles existence
5.	Sun et al.		Detection: 2.5–4 M Operating temperature: 30–6 °C	Two cathodes, two current signal Pulse-mode operated	Expensive Pt-C as sensing materials
6.	Sparks et al.		Detection: 0.6–3 M Operating temperature: 5–50 °C	A microfluid chip MEMS based methanol sensor	External electronic required to amplify signal
7.	Park et al.		Detection: 1.0×10^{-4} M Operating temperature: 20–80 °C	Eliminate CO adsorption using silicon epoxy film	Suitability in DMFC system not determined
8.	He et al.		Sensitivity: $(3.03 \pm 0.09) \times 10^{-3}$ °C^{-1} Operating temperature: 20–100 °C	Thin film gold thermistor embedded in parylene film.	Thickness of parylene and ability to detach from Nafion will affect the sensor.
9.	Inman et al.	Emission of gas	Temperature: 60 (±0.6 °C) Chromium doped aluminium oxide (ruby) decay detection using optical fibre	Measure in-situ plane temperature	Optical fibre has to be inserted into the cell might damage internal of cell.
10.	David et al.		Sensitivity: 10.7 pm °C^{-1} Use in-fibre grating (FBG) sensor	Good temporal responds to dynamic load	Physical insertion inside the cell
11.	Burggman et al.		Use micro particle image velocimetry in determine CO_2 bubbles movement	In situ detection of flow of CO_2	Use of bulky microscope to capture the image
12.	Kirby et al.		Detection: 50 ppm CO min. to 100 ppm	Suitable design for incorporation into the stack Reduce the Pt to increase sensitivity, low cost.	At high concentration, hard to regain current baseline due to short air recovery period
13.	Van Der Wal et al.		Detection: 0.2–0.8 ppm CO. Response time: 20–90 s	Usage of dry Nafion and wet Nafion as sensor	Lifetime was not sufficient for dry Nafion
14.	Yasuda and Shimidzu		Response time: 30 s Range: 0–2000 ppm Sensitivity: 0.04 nA/ppm	PEM film covered with perfluorocycloether enhanced stability and CO oxidation rate	Nafion film is sensitive to water
15.	Holt et al.		Sensitivity: 50–60 °C Fast response times (~1 s)	CO detection by monitoring resistance changes of the film in a simulated reformed gas, rich in H_2	Presence of water vapors in the gas stream greatly damages the sensor

concentration. A low current density is obtained at low methanol concentrations. Thus, a methanol concentration sensor is essential to prevent the aforementioned problems from arising in DMFCs.

There have been several studies on developing methanol sensors for DMFCs; for example, Jeng et al. [22] developed a fuel-cell-type methanol sensor with an unsymmetrical anode and cathode set, as shown in Fig. 5. The sensor could be operated using a flowing or stagnant fuel solution for temperatures ranging from 20 °C to 80 °C. However, the flowing system could not prevent gas-blockage for this case. Additional problems, such as obstructions in the gas flow and variations in the fuel supply, can arise. The other type of methanol sensor depends on a diffusion-limited concentration-dependent oxidation current under a constant anodic potential. Geng et al. [6] developed a sensor that produced an alternating pulse signal. A methanol solution was fed simultaneously to both electrodes, and the methanol concentration was determined from the potentiostat readings. When hydrogen was produced at both electrodes alternately, the electrodes underwent a self-cleaning process that maintained the catalyst. However, the alternating pulse sensor increased the complexity of the power control, which would be difficult to implement in portable DMFC systems.

Yan et al. [23] developed a miniaturised sensor in which the DMFC was coupled to real-time monitoring of the concentration (see Fig. 6). The current increased with the concentration up to a value of 2.5 M, after which the current decreased upon further increases in the concentration. This phenomenon is called concentration saturation. However, the paper did not discuss optimisation and performance aspects. Lee et al. [24] developed a miniaturised methanol sensor with a gas diffusion backing layer (GDBL) and housing for the physical unit (see Fig. 7). The authors demonstrated that the sensor could detect concentration differences for power rates at low as 0.5 V (for a miniaturised DMFC) and that the GDL had little effect at low power. However, the repercussions of not using the GDL in managing gas bubbles, which is a significant issue in DMFC operation, were not clearly examined.

Sun et al. [25] fabricated a twin-MEA-assembled sensor for methanol concentration using face-to-face anodes (see Fig. 8) to provide two current signals simultaneously. Pulsed amperometric detection (PAD) method was implemented by applying a repeating potential versus time waveform to the working electrode for flow through the detector. The sensor showed significant improvements in its response and stability using PAD over a potentiostatic

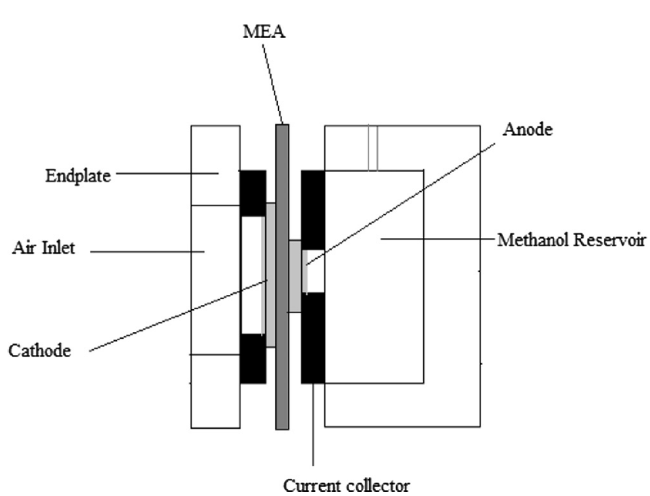


Fig. 5. The sensor has asymmetric electrode set which uses ambient air as oxygen [22].

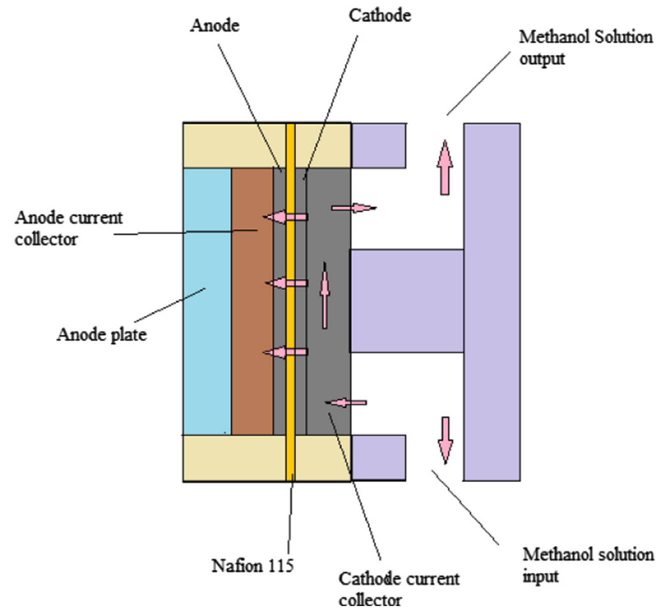


Fig. 6. Sectional view of the miniaturized sensor [23].

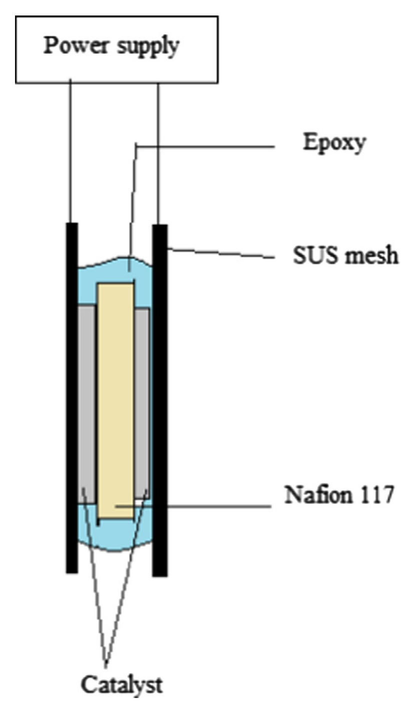


Fig. 7. The sensor assembly consisting of the catalyst coated Nafion membrane (CCM) [24].

mode and exhibited a slightly linear degradation rate of 2.9 mA h^{-1} during a long-time test. Other techniques have also been used to detect the methanol concentration. For instance, Seok et al. [26] used *I–V* characteristics based on changes in the Pt thickness as function of the methanol concentration. A thin composite Nafion membrane was used as an electrolyte was in the fabricated methanol sensor. The current increased with the methanol concentration; the electric current increased as the catalysing electrode became thinner. Mao and Krewer [27] used total harmonic distortion (THD) spectra to determine the methanol concentration. The THD value varied monotonically with the methanol concentration at

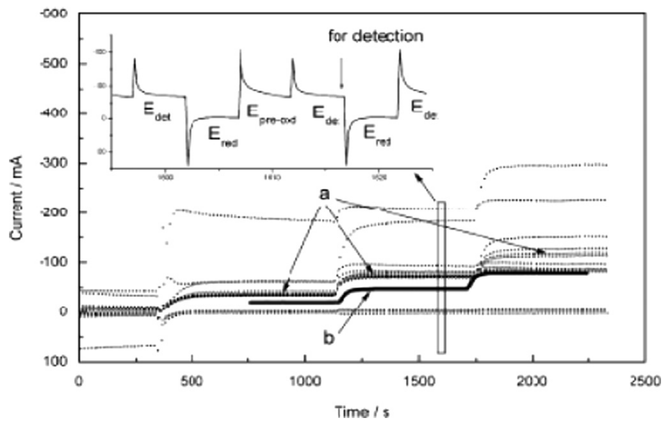


Fig. 8. Sensor response current vs. elapsed time [25].

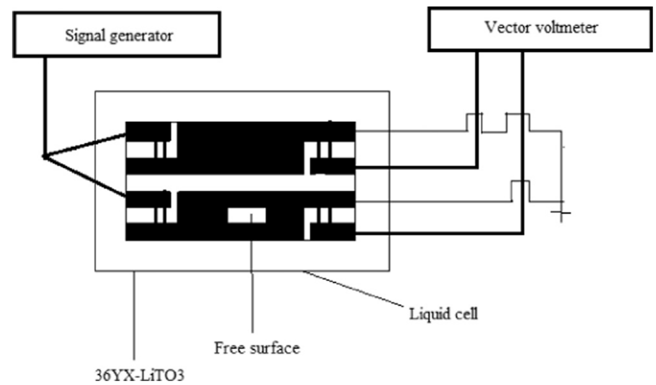


Fig. 10. Schematic illustration of the SH-SAW sensor for detecting liquid electrical properties with the signal generator and vector voltmeter [33].

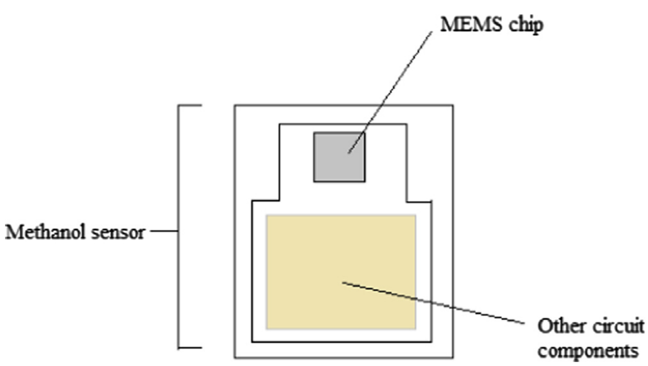


Fig. 9. MEMS based methanol concentration sensor [29].

certain frequencies. This correlation was used to determine the methanol concentration level from the THD values for a DMFC.

Sparks et al. [28] developed a micro electro mechanical systems (MEMS) sensing chip to monitor and control the methanol concentration (see Fig. 9); however, relatively high flow rates could not be used with a stand-alone micro-tube because of the high pressure drop. Although a bypass package design can facilitate the use of higher flow rates, the performance of the MEMS-based DMFC will remain unsatisfactory because of the incompatibility between the carbon electrodes and MEMS technology [30]. MEMS technology has also been used in research studies on thermal sensors [31,32]. Kondoh et al. [32] used a shear horizontal surface acoustic wave device (SH-SAW) to develop a methanol sensor. Interdigital transducers (IDTs) and a sensing surface were fabricated using lithography on a SH-SAW substrate (which was a $LiTaO_3$ single crystal in this case). The wave characteristics were numerically calculated by measuring the electrical properties. A decrement in the methanol concentration indicated a low permittivity, and a surface skimming bulk wave (SSBW) was observed. However, the conductivity was significantly affected by the formation of formic acid (Fig. 10).

3.2. Heat and water management for thermal sensors

Schröder et al. [33] fabricated a new arrangement on carbon cloth to investigate the effect of GDL wettability on DMFC performance (see Figs. 11 and 12). In this fabrication scheme, a printed circuit board (PCB) was inserted at the anode side to forma current and temperature measurement system. For a segmented anode, the anode wettability was only a minor effect because no flooding occurred at the cathode and because the cell performance was enhanced. However, for a segmented cathode, the untreated section initially absorbed water rapidly, but the hydrophobic section of the cathode expelled this water over time. There was a high probability of flooding when water droplets formed at the flow channel in the cell. Thus, this is not a suitable configuration for the cathode because the higher the current density, the greater the quantity of water that is produced in the cathode gas electrode. High resolution radiography was performed simultaneously with the measurement of the local current distribution to analyse the GDL wettability; however, this method did not work for the cathode GDL.

Guo et al. [34] investigated the thermal behaviour of a methanol sensor (see Fig. 13) using a zero-dimensional mathematical model, which could be justified because of the small temperature gradient in three different operation modes: constant resistance, constant current and constant voltage. When the methanol supply was continuous, the temperature rose to a stable equilibrium value. In a non-continuous operation mode, the temperature rise could be described by combining the temperature behaviour for the continuous operation mode with linear function. The temperature rise curves followed the zero-dimensional model. The maximum temperature rise and the methanol concentration were fit by linear functions for each test case. The heat production rate was linear in the methanol concentration (0.5–10.0 mol/L). He et al. [36] used a patterned thin film gold thermistor embedded in a 16-μm thick parylene film, which was laminated in a Nafion electrolyte layer using a microfabrication technique, to perform a real-time temperature measurement with an in- and out-flow (see Fig. 14). Poor thermal management resulted in the membrane drying out or flooding of the diffusion media; a long-term effect of high temperatures was the decomposition of the sulphonate group, which could increase the fuel crossover rate through the electrolyte and degrade the cell performance. The temperature sensitivity was reported to be an order of magnitude higher than for conventional micro-thermocouples. Micro-fabrication techniques can also facilitate the accurate placement of a temperature sensor within a fuel cell. These techniques have no significant effects on the local temperature distribution.

Inman et al. [36] constructed a thermal sensor using the lifetime decay method for phosphor thermometry to measure the temperature in the cell (see Fig. 15). The optical temperature was accurately measured within an error of $\pm 0.6\ ^{\circ}C$, which was determined by comparison to a precision resistance temperature detector (RTD). However, measuring the GDL temperature directly required that an optical sensor protrude through the end-plate, which could have affected the cell interior. Wang et al. [11]

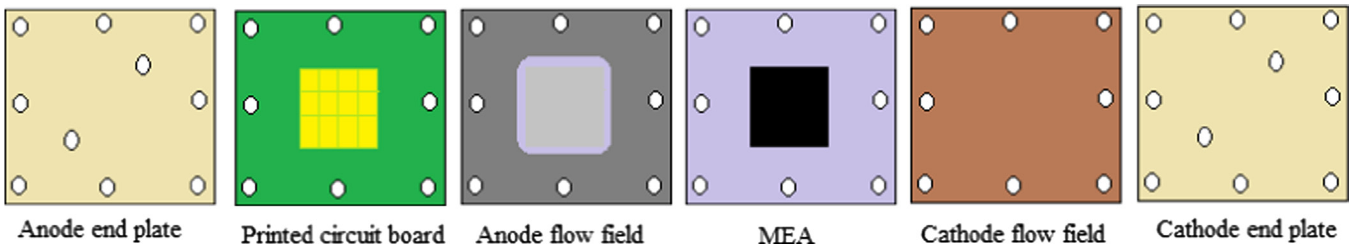


Fig. 11. Assembly of Schroder et al. test cell [34].

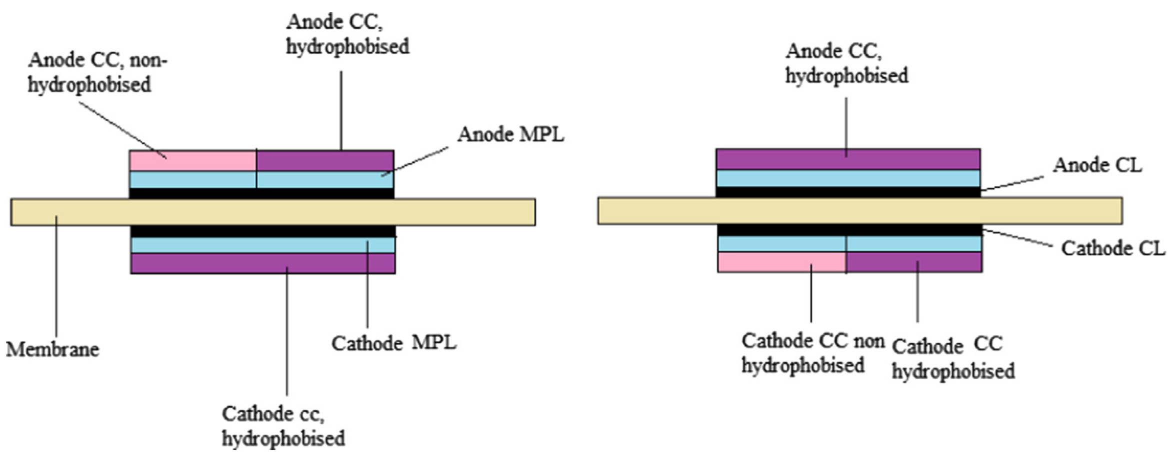


Fig. 12. New arrangement of carbon cloth [34] left picture, partitioning Anode GDL on the right partitioning of cathode GDL.

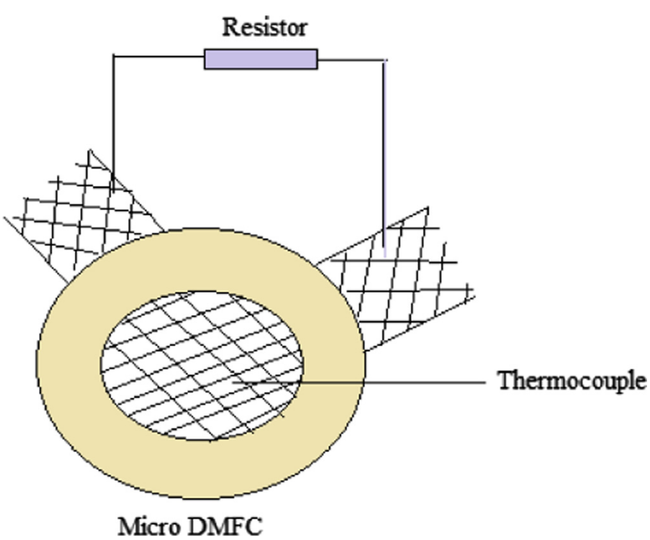


Fig. 13. Micro methanol concentration sensor proposed by Guo et al. [34].

developed a method to locate hot spots (locally high temperature regions) using an infra-red camera. The anode side was viewed by the camera under different operating temperatures and current densities. A barium fluoride window was used to modify the anode polar plate to render it transparent for camera viewing. Therefore, anode polar plate could only be used for a single cell or the cell at the end of a stack. The current densities increased as the water production at the cathode increased. Consequently, the emissivity became unstable. David et al. [2] used an in-fibre Bragg grating (FBG) sensor to measure the internal temperature. The FBG consisted of a short segment of an optical fibre, which produced photo-induced refraction. Light interference resulted in peaks at

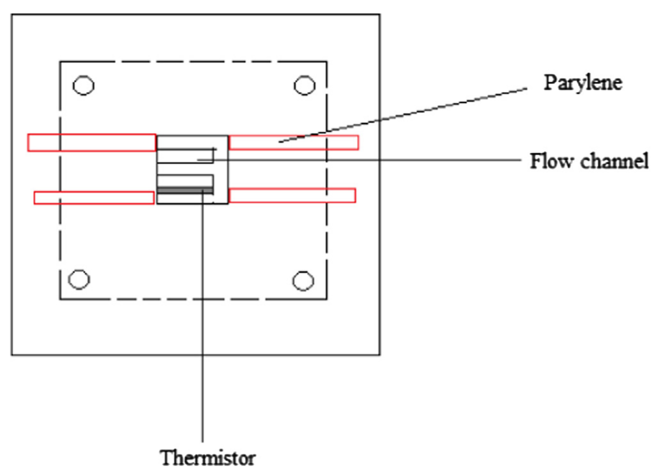


Fig. 14. Temperature sensor design by He et al. [35].

wavelengths known as the Bragg wavelengths. FBGs are hydrophobic and do not affect electromagnetic interference.

3.3. Flow sensors

Burgmann et al. [37] reported that the cell performance was enhanced by large CO_2 bubbles. The authors investigated the effect of the presence of large CO_2bubbles in the fuel cell by visualising the motion of the gas bubbles on a line. The bubbles appeared larger at high current densities and formed a moving slug that stopped the forced flow of methanol. The residual methanol in the GDL reacted, but no fresh methanol was added. The reaction resulted in an increase in quantity of CO_2 even before the slug passed the channel. This behaviour resulted in a voltage drop across the channel.

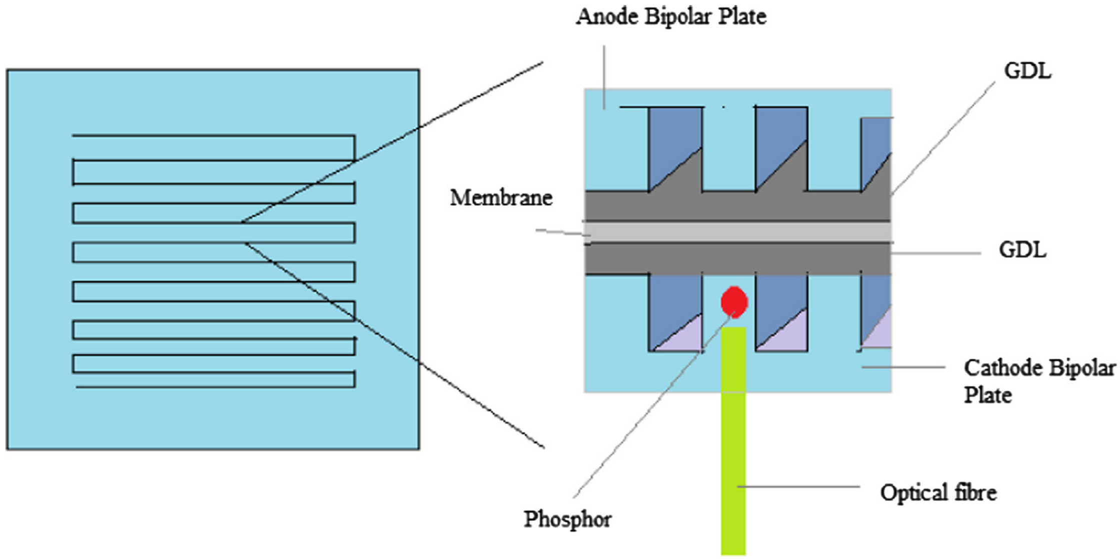


Fig. 15. Diagram of sensor placement in PEM fuel cell [37].

3.4. Gas sensor emissions

The incomplete oxidation of methanol with water resulted in CO production at the anode. Instead of releasing CO_2, CO was released and adsorbed at the electrode surface on the catalyst layer. The catalyst layer can be poisoned by CO adsorption, damaging the electrode. Thus, it is important to detect CO to provide feedback to the fuel cell and protect the catalyst layer.

Kirby et al. [3] developed a sensor for detecting carbon monoxide (CO) concentrations as low as 50 ppm in a PEM fuel cell. However, an additional method was needed to raise the temperature to thermally drive CO from the Pt surface. In a study by Van Der Wals et al. [38], a Nafion was used to fabricate a CO sensor. Nafion is available as sheets of different equivalent weights (i.e., the weight of the resin per ion exchange site). Nafion can be deposited on surfaces using solvent casting. Wet Nafion sensors have been shown to be more stable than dry Nafion sensors. A humid sensor exhibited higher proton conductivity than a dry sensor. Three Teflon-bonded platinum black electrodes were integrated onto a partly permeable ceramic substrate. The sensor included a Teflon gas diffusion membrane and a recast Nafion electrolyte. The working electrode (WE) and the counter electrode (CE) were fixed using laser-drilled holes, and the reference electrode (RE) was positioned at the impermeable section of the substrate. A specified amount of CO was added to synthetic air; the CO concentration was then detected by the change in the potentiometer readings. The dry Nafion sensor was cheapest and easiest to use of all of the sensors, but had a short lifetime. The wet Nafion sensor in an acidic solution was more stable and less affected by the temperature than the dry sensor.

Yasuda and Shimidzu [39] also fabricated a CO sensor with a planar electrochemical structure. The three electrodes, the WE, the CE and the RE, were placed side-by-side on a glass substrate. The results showed that oxidised Pt was reduced at the WE. The current was larger when CO was present. This sensor is suitable for measuring CO permeation or a CO oxidation rate (see Fig. 16). Holt et al. [40] used copper chloride to detect CO by monitoring the resistance changes in a film. The presence of CO reduced the resistance, which was recovered when the CO was removed. The CO sensitivity was lost for temperatures above 75 °C because of water vapour formation. The films appeared slightly green because of the reaction between CO, CuCl and water.

4. Sensor-less approach

Methanol crossover is considered to be the most severe limitation of DMFCs. There has been no solution to this problem to date other than to use low methanol concentrations in DMFCs. However, insufficient fuel results in a lower output power. Many studies have been conducted on electrochemical sensors with satisfactory results. However, an electrochemical sensor cannot provide the user with information on the amount of residual fuel. An algorithm for sensor-less methanol control was designed to regulate the methanol concentration and the fuel consumption rate [41]. The algorithm combined individual algorithms that interpolated between constant concentration surfaces of (I, V, T), (M', I, T) and (W, I, T), where' denotes the methanol consumption rate and W denotes the net water consumption at the anode. The authors corrected for the performance decay by air-starving the cathode to use up the residual oxygen from the oxidation of the crossover methanol.

$$M'_u = \sum_{k=1}^{n} \left(\prod_{\substack{i=1 \\ i \neq k}}^{n} \frac{C_{M,u} - C_{M,i}}{C_{M,k} - C_{M,i}} \right) \times M'_k \tag{4}$$

$$W'_u = \sum_{k=1}^{n} \left(\prod_{\substack{i=1 \\ i \neq k}}^{n} \frac{C_{M,u} - C_{M,i}}{C_{M,k} - C_{M,i}} \right) \times W'_k \tag{5}$$

The M' and W' values were calculated using methanol concentrations up to 6.0 vol%. This algorithm controlled the methanol concentration at 5.0 ± 0.5 vol% for a total liquid volume at 8.0 vol%. Chang et al. and Chen et al. [7,42] developed a sensor-less fuel feeding system. The control scheme used an impulse response based on discrete time fuel injection (IR-DTFI) algorithm to provide easier and faster control of the fuel feeding. The DMFC operating characteristics, such as the potential, the current and the power, were measured by regulating the feed and the methanol concentration. The methanol concentration was controlled by the injection quantity, which was governed by the pulse width. The pulse width was set using a programmable DC power supply that drove a fuel pump. Increasing the pulse width increased the power oscillations. Although the effect of this

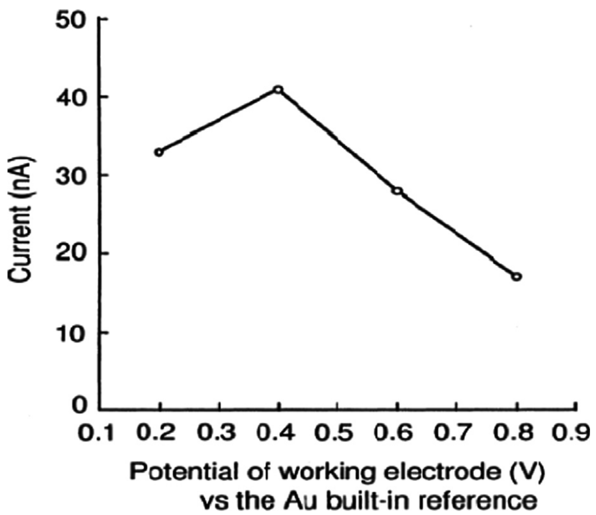


Fig. 16. Relationship of CO oxidation current and applied potential at 20 °C [40].

control scheme on MEA degradation has not been clearly proven, a demonstration of a DMFC-powered DVD player showed that the control system was reliable. Jung et al. [43] also a designed sensor-less methanol concentration system (SLCC) using an algorithm based on the methanol consumption rate. Consumption rates from experiments performed under various operating conditions were used to construct a database to predict the methanol consumption rate (which was the dependent variable). The consumption rate was the sum of the electrochemical oxidation rate and the methanol crossover rate. The current and the temperature were the independent variables. A CO_2 analyser was attached to the cathode to measure the CO_2 concentration in the air outflow from the cathode, from which the methanol crossover was determined.

5. Current issues

As described in afore mentioned literature, researchers have expended tremendous efforts to improve DMFC performance. Despite all of the advantages offered by DMFCs, they are still not ready to be commercialised because of high fabrication costs and operational difficulties. The main problem in DMFC operation is methanol crossover. Methanol crossover reduces the output voltage considerably. Methanol crossover also damages the cell. CO emissions from the incomplete oxidation of methanol and water also affect the cell performance. CO adsorbs to Pt catalyst particles, interrupting their catalytic activity. CO also poisons the electrode, thereby damaging the whole cell. The only solution is to change the electrode. Heat and water management of DMFCs is vital for improving cell performance. Heat management and water management are closely interrelated. The water in DMFCs is removed by vaporisation (using heat). Water problems manifest as flooding or dry conditions [35,36]. When conditions are too dry, proton conduction is disturbed; flooding increases the crossover rate because methanol is forced to react with water. However, flow considerations are not serious issues in DMFC operation. This statement can be confirmed byte amount of literature available on flow considerations [38]. The sensor-less approach is discussed next. The sensor-less method is a method that can be found in literature for enhancing cell performance without the use of a sensor. This method can realise low-cost and high efficiency DMFCs. The method primarily uses algorithms to regulate certain conditions. Existing studies on sensor-less methods have mainly attempted to find solutions for a methanol concentration and feeding system [7,22,43].

6. Conclusions and suggestions

In this review, various types of sensor have been described. The literature reviewed here highlights the significance of using sensors in DMFCs. These sensors are important for improving DMFC performance and enabling DMFC commercialisation. It is no doubt that electrochemical sensor is most suitable for DMFC system. The similar base concept of DMFC and the electrochemical sensor provide simpler fabrication. It is known that physical sensor will give more stable outcome and the whole cost will be slightly less than electrochemical sensor, however, the physical sensor is bulky and it have to be outside of the cell. Despite the whole cost that seems slightly less, the maintenance cost also will be higher. This give the advantage to the electrochemical sensor with less maintenance cost. The other type of sensor is sensor less approach. This is usually related to the application of mathematical equation which is far more complicated. Despite that, sensor less approach provides more accuracy on the data and in situ evaluation due to the existing database. Besides, it will be simpler without the sensor itself. To date, many of researches have done the optimizing on the existing electrochemical sensor specifically in material aspect. Apparently, the nanomaterial is the latest research on building the electrodes.

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